

CLAIMS

1. A method for producing micro emulsions dissolved or dispersed in a compressed fluid in a near critical or a supercritical state comprising:
5
 - introducing a first fluid into a pressurised vessel;
 - introducing one or more surfactant(s) into said pressurised vessel;
 - introducing a second fluid into said pressurised vessel;
 - promoting formation of micro emulsions of said second fluid within said first
10 fluid present in said pressurised vessel.
2. A method according to claim 1 further comprising withdrawing in at least part time of said method a fluid stream comprising said micro emulsions suspended, dispersed or dissolved in said fluid being in a near critical or supercritical state.
15
3. A method according any of the claims 1-2, wherein said promotion of formation of micro emulsions is performed after introduction of said fluids and surfactant(s) into said pressurised vessel.
- 20 4. A method according to any of the claims 1-3, wherein one of the fluids is compressed CO₂.
5. A method according to claim 4, wherein said compressed CO₂ is a compressed liquid.
25
6. A method according to claim 5, wherein the compressed CO₂ is a supercritical fluid.
7. A method according to any of the claims 1-6, wherein one of the fluids is water
30 or contains water.
8. A method according to claim 7, wherein said water or water mixture further contains one or more substances preferably being dissolved and/or dispersed therein.
35
9. A method according to any of the claims 7-8, wherein said one or more substances comprises polar molecules and/or polarizable molecules and/or non-polar, non-volatile molecules.

10. A method according to claim 9, wherein said one or more substances is substantially insoluble in said compressed CO₂.
- 5 11. A method according to any of the preceding claims, wherein one of the fluids is an organic solvent, such as an oil.
12. A method according to any of the preceding claims, wherein said CO₂ containing fluid further comprises at least one co-solvent.
- 10 13. A method according to claim 12, wherein the co-solvent is selected from the group consisting of alcohol, water, ethane, ethylene, propane, butane, sulfur-hexafluoride, nitrous oxide, chlorotrifluoromethane, monofluoromethane, methanol, ethanol, DMSO, isopropanol, acetone, THF, acetic acid, ethyleneglycol, polyethyleneglycol, N,N-dimethylaniline etc. and mixtures thereof.
- 15 14. A method according to any of the preceding claims, wherein said CO₂ containing fluid further comprises one or more surfactant(s), comprising a CO₂-philic portion and a CO₂-phobic portion.
- 20 15. A method according to claim 14, wherein said surfactant(s) is/are chelate(s) and/or fluorinated surfactant(s), and/or perfluoropolyether surfactant(s), and/or fluoroetherfluoracrylate surfactant(s) and/or siloxane surfactant(s).
- 25 16. A method according to any of the claims 14-15, wherein said surfactant(s) is/are selected from the group consisting of hydrocarbons and fluorocarbons preferably having a hydrophilic/lipophilic balance value of less than 15, where the HLB value is determined according to the following formula: $HLB = 7 + \text{sum}(\text{hydrophilic group numbers}) - \text{sum}(\text{lipophilic group numbers})$.
- 30 17. A method according to any of the claims 14-16, wherein the amount of said surfactant(s) compared to the amount of water corresponds to a concentration in the range 0,01 to 10 weight %, such as a concentration in the range 0,05 to 5 weight %, preferably a concentration in the range 0,1 to 3 weight %, and advantageously a concentration in the range 0,5 to 2 weight %.
- 35 18. A method according to any of the claims 14-17, wherein the molar ratio of water to said surfactant(s) is at least 5:1, such as a molar ratio of at least 10:1, pref-

erably a molar ratio of at least 20:1, such as a molar ratio of at least 30:1, and advantageously a molar ratio of at least 50:1 such as at least 100:1.

19. A method according to any of the claims 14-18, wherein the molar ratio of compressed surfactant to the dissolved and/or dispersed molecules in said second fluid is at the most 100:1, such as at the most 50:1, and preferably at the most 30:1 such as at the most 10:1.
20. A method according to any of the preceding claims, wherein the pressure of at least one of said fluids is in the range 50-500 bars, preferably in the range 85-500 bars, such as in the range 100-300 bars.
21. A method according to any of the preceding claims, wherein the temperature in said pressurised vessel is maintained in the range 20-500 °C, such as 30-450 °C, and preferable in the range 35-200 °C, and more preferable in the range 40-150 °C.
22. A method according to any of the preceding claims, wherein said pressurised vessel is operating at a substantially constant pressure.
23. A method according to any of the preceding claims, wherein said emulsion formed is a micro- or nano emulsion.
24. A method according to claim 23, wherein the diameter of the core(s) of said micro- or nano emulsion(s) is/are at least partly controlled by controlling the density of said fluid(s) present within said pressurised vessel.
25. A method according to any of the claims 23-24, wherein said micro emulsion(s) formed comprises a water core(s).
26. A method according to claim 25, wherein the diameter of said water core(s) is/are at the most 5 micron, such as a diameter of at the most 1 micron, preferably a diameter of at the most 500 nm such as a diameter of at the most 250 nm, and more preferably a diameter of said water core(s) of at the most 100 nm such as a diameter of at the most 50 nm, and advantageously the diameter of said water core(s) is below 30 nm.
27. A method according to any of the claims 23-26, wherein said micro emulsion(s)

formed is continuously withdrawn from said pressurised vessel.

28. A method according to any of the claims 25-27, wherein said micro emulsion(s) containing fluid being withdrawn from said pressurised vessel is used to dissolve and/or extract substances from a material in a device outside such as downstream of said pressurised vessel.
29. A method according to any of the claims 25-27, wherein said water core comprises dissolved and/or dispersed substances.
30. A method according to claim 29, wherein said fluid(s) containing said micro emulsion(s) is/are used as carrier(s) for transporting dissolved and/or dispersed species to an external device.
31. A method according to any of the preceding claims, wherein two or more micro emulsions of different compositions is produced in separate pressurised vessels and the fluids containing said micro emulsions are combined in an external device.
32. A method according to claim 31, wherein said two emulsions of different composition are formed using at least two different surfactants.
33. A method according to claim 32, wherein said surfactants are designed with electrostatic forces so as to facilitate contact of micelles of different type and to reduce merging of micelles of same type.
34. A method according to claim 33, wherein said electrostatic forces are introduced by including a molecular charge displacement in the lipophilic part of the surfactant.
35. A method according to claim 34, wherein said molecular charge displacement are obtained by introducing polarity from organic molecular groups selected from halogenated alkyls and/or halogenated aryls and/or aldehydes, and/or ketones and/or ethers and/or hetero-cyclic structures containing oxygen, nitrogen and/or sulphur and/or amides and/or mercaptanes.
36. A method according to any of the preceding claims, wherein said micro emulsion(s) is/are used as nanoreactors for synthesis of a nanoparticle materials.

37. A method according to claim 36, wherein at least one chemical reaction is occurring in said micro emulsions.
- 5 38. A method according to any of the claims 36-37, wherein said micro emulsion(s) is/are used as template(s) for controlling said particulate material into a specific shape, size and/or structure.
- 10 39. A method according to any of the claims 31-38, wherein the average size of said nanoparticle material formed is maximum 5000 nm, such as an average size of maximum 500 nm, preferably the average size is maximum 100 nm, and most preferably the average size is maximum 30 nm, such as maximum 15 nm.
- 15 40. A method according to any of the claims 31-38, wherein the average size of said nano particle material formed is in the range 0,1-30 nm, such as in the range 1-10 nm.
- 20 41. A method according to any of the claims 36-40, wherein said synthesis of said nanomaterials is at least partly controlled by controlling the temperature and/or the pressure of the fluid(s) during said synthesis.
- 25 42. A method according to any of the preceding claims, comprising re-circulating in at least part time of the method at least part of a fluid or fluid mixture present in said pressurised vessel, the re-circulating comprising withdrawing from the vessel at least part of a fluid contained in said vessel and feeding it to a re-circulation loop and subsequently feeding it back to said pressurised vessel.
- 30 43. A method according to claim 42, further comprising the step of controlling the temperature of the fluid in the re-circulation loop.
- 35 44. A method according to any of the claims 42-43, wherein the fluid volume being withdrawn from said vessel to said re-circulation loop corresponds to exchange of at least 0,1 vessel volume per minute such as at least 0,25 vessel volumes per minute, preferably the fluid volume corresponds to exchange of at least 0,5 vessel volumes per minute, and even more preferably exchange of at least 1 vessel volume per minute and advantageously the fluid volume being withdrawn corresponds to exchange of at least 2 vessel volumes per minute such as exchange of at least 5 vessel volumes per minute.

45. A method according to any of the claims 42-44, wherein said re-circulation loop comprises at least one mixing zone for promoting formation of micro emulsion(s).
- 5 46. A method according to any of the claims 42-45, wherein said mixing zone(s) in said re-circulation loop comprise(s) a static mixer.
- 10 47. A method according to any of the claims 42-46, wherein said mixing zone(s) in said re-circulation loop comprises a pressurised container with a high shear rate mixer.
48. A method according to claim 47, wherein said high shear rate mixer comprises a motor driven mixer such as an impeller such as a propeller or turbine rotor.
- 15 49. A method according to claim 48, wherein impeller comprises a stator and a rotor.
- 20 50. A method according to claims 49, wherein said high shear rate mixing is obtained by maintaining the distance from the surface of rotor to the surface of the stator is below 5 mm such a distance of below 2,5 mm, and preferably below 1 mm such as below 0,5 mm, and advantageously below 0,2 mm.
- 25 51. A method according to claim 47-50, wherein said high shear rate mixer in said pressurised container in said re-circulation loop comprises a rotor rotating with a speed of at least 5000 rpm such as a speed of at least 10000 rpm, and preferably at a speed of at least 15000 rpm such as a speed of at least 20.000 rpm, and advantageously the rotor is rotating at a speed of 24000 rpm or more.
- 30 52. A method according to any of the claims 42-51, wherein said re-circulation loop comprises ultrasonic generating means for generating ultrasonic waves or vibration waves in/of said fluid being withdrawn to said recirculation loop.
- 35 53. A method according to claim 52, wherein the frequency of said ultrasonic generating means are in the range 20 kHz to 10 MHz such as in the range 20 kHz to 2 MHz and preferably in the range 20 kHz to 50 kHz such as in the range 40-50 kHz.

54. A method according to any of the claims 52-53, wherein said ultrasonic generating means comprises a piezoelectric or magneto-restrictive structure.
55. A method according to any of the claims 52-54, wherein said ultrasonic generating means are placed within said pressurised container within said re-circulation loop.
56. A method according to any of the claims 42-55, wherein said mixing in said one or more mixing zone(s) for promoting formation of said micro emulsions, is at least partly provided by atomizing said fluid being withdrawn to said re-circulation loop by spraying said fluid into said pressurised container in said re-circulation loop through one or more nozzles.
57. A method according to claim 56, wherein said one or more nozzles is/are ultrasonic nozzles.
58. A method according to claim 56, wherein said one or more nozzles comprise(s) one or more membranes situated within said pressurised container within in said re-circulation loop.
59. A method according to claim 58, wherein said one or more membranes comprises the inner wall of said pressurised container within said re-circulation loop.
60. A method according to any of the preceding claims, wherein said pressurised vessel is an agitated vessel.
61. A method according to claim 60, wherein said agitation is provided by a motor driven mixer such as an impeller.
62. A method according to claim 61, wherein said impeller is rotating with a speed in the range 100-5000 rpm, such as an impeller with a rotating speed in the range 250-3000 rpm, and preferably in the range 500-2000 rpm.
63. A method according to any of the preceding claims, wherein said pressurised vessel comprises ultrasonic generating means.
64. A method according to any of the claims 60-63, wherein said pressurised vessel further comprises one or more atomising nozzles.

65. A method according to claim 64, wherein said atomising nozzles comprise at least one ultrasonic nozzle.
- 5 66. A method according to any of the claims 42-65 comprising withdrawing from an agitated pressurised vessel at least part of a fluid or a fluid mixture contained in said agitated pressurised vessel and feeding it to a re-circulation loop, said re-circulation loop comprising a pressurised container comprising a high shear rate mixer for promoting formation of micro emulsions, and subsequently feeding
10 said fluid or fluid mixture back to said pressurised vessel.
67. A method according to claim 66, wherein said second fluid and/or said surfactant(s) are introduced into said pressurised container in said re-circulation loop.
- 15 68. A method according to claim 67, wherein said second fluid and/or said surfactant(s) are premixed prior to introduction into said pressurised container.
69. A method according to any of the preceding claims, wherein said pressurised vessel comprises a plurality of hollow tubular members, at least part of the walls
20 of said hollow tubular members comprising membranes, the plurality of hollow tubular members defining interstices therebetween allowing for flow and
- Contacting the outer surface of a plurality of said hollow tubular members with a first fluid, and
25
 - Contacting a second fluid with the inner surface of said hollow tubular members, at least part of said second fluid is permeating said membrane walls forming a plurality of emulsion(s) of said second fluid dispersed in said first fluid.
30
70. A method according to claim 69, wherein the membrane part of said hollow tubular members comprises porous membranes.
71. A method according to claim 70, wherein the pore size of said porous membranes is in the range 0,001-100 microns, such a pore size in the range 0,01-10
35 micron, and preferably having pores in the range 0,01-0,2 micron.
72. A method according to any of the claims 69-71, wherein the diameter of said

water core in the emulsions formed is in the range 0.001-30 times the diameter of the pores of the membrane part of said hollow tubular members, such as in the range 0.01-15 times the diameter of the pores of the membrane part of said hollow tubular members, and preferably in the range 0.1-10 times the diameter of the pores of said hollow tubular members.

73. A method according to any of the claims 69-72, wherein the pressure of the fluid(s) contacting the inner surface of said hollow tubular members is higher than the pressure of the first fluid.
74. A method according to claim 73, wherein the pressure differences between the fluid(s) contacting the inner surface of said hollow tubular members and the first fluid is in the range 0,01-100 bars, such as in the range 0,1-50 bars, and preferably in the range 0,1-20 bars such as in the range 0,1-10 bars.
75. A method according to any of the claims 69-74, wherein said hollow tubular members comprise hollow fibres.
76. A method according to any of the claims 69-75, wherein said membrane is a ceramic or polymeric membrane.
77. A method according to any of the claims 69-76, wherein the temperature profile within said pressurized vessel is controlled by controlling the temperature and flow rate of at least one fluid contacting the inner surface of said hollow tubular members.
78. A method according to any of the claims 69-77, wherein said tubular members comprise two separate set of hollow tubular members, both sets of said hollow tubular members comprising an inlet and an outlet plenum communicating with the outside of said pressurized vessel, and wherein two separate fluids may be contacted with the inner surface of said hollow tubular members, and wherein two different emulsions of said fluids in said first fluid contacting the outer surface of said hollow tubular members are formed.
79. A method according to any of the preceding claims, wherein the first fluid containing said micro emulsion(s) is/are expanded in a device external to the pressurised vessel.

80. A method according to claim 79, wherein the first fluid is rapidly expanded through one or more nozzles using a RESS or a RESOLV technique.
81. A method according to any of the claims 79-80, wherein the content of said micro emulsions formed is/are deposited on the surface of a substrate such as on the surface of solid material.
82. A method according to claim 81, wherein said material being deposited comprises an inorganic substance.
83. A method according to claim 81, wherein said material being deposited comprises a pharmaceutical substance such as a medical agent, a biologically active material, an antigen, an enzyme, a therapeutic protein or a therapeutic peptide.
84. A method according to any of the claims 81-82, wherein said material being deposited comprises one or more metal(s) and/or one or more semi-metal(s), or one or more metal oxide(s) and/or one or more semi-metal oxide(s).
85. A method according to claim 81, wherein said material being deposited comprises an electroceramic material.
86. A method according to claim 81, wherein said material being deposited material comprises a semi-conducting material.
87. A method according to any of the claims 81, wherein said material being deposited comprises a magnetic, ferromagnetic, paramagnetic, or supermagnetic material.
88. A method according to any of the claims 81-87, wherein the deposited material constitutes a layer of primary particles having an average diameter of the most 30 nm such as at the most 20 nm, such as at the most 10 nm.
89. A method according to claim 88, wherein the thickness of said layer is at the most 500 nm, such as at the most 100 nm, and preferably at the most 50 nm such as at the most 25 nm.
90. A method according to any of the claims 81-89, wherein said solid material being treated comprises a tape cast for tape casting.

91. A method according to any of the claims 81-89, wherein said treated solid material comprises a catalyst material.
- 5 92. A method according to any of the claims 81-89, wherein said treated solid material comprises a ceramic membrane.
93. A method according to any of the claims 81-89, wherein said treated solid material comprises a fuel cell material.
- 10 94. A method according to any of the claim 81-89, wherein said treated solid material comprises a photolithographic lens or mask.
95. A method according to claim 81, wherein said treated solid material comprises a
15 medical and/or a pharmaceutical article.
96. A method according to any of the preceding claims, wherein said external device is an apparatus for producing fine particles.
- 20 97. A method according to claim 96, wherein one or more additional fluids containing micro emulsions with substances dissolved and/or dispersed therein, is introduced into said external device, so as to perform a micro encapsulation of said fine particles formed.
- 25 98. A method according to claim 96, wherein said external device contains a solvent and said fine particles are collected as a dispersion of said fine particles within said solvent.
99. A method according to claim 96, wherein said solvent further comprises a reac-
30 tant for said particle formation process.
100. A method according to any of the preceding claims, wherein said primary particles formed comprise one or more pharmaceutical and/or biological material(s).
- 35 101. A method according to any of the preceding claims, wherein said material being deposited and/or collected comprise one or more metal(s) and/or one or more semi-metal(s) or a combination thereof.

47

102. A method according to claim 101, wherein the electrolyte dissolved and/or dispersed within said micro emulsions is/are a reactant(s) in a supercritical sol-gel reaction.

5 103. A method according to any of the preceding claims, wherein said fine particles formed comprises oxide(s) such as metal oxide(s) or semi-metal oxide(s).

104. A method according to claim 103, wherein said oxides is/are a thermoelectric material or a precursor for production of a thermoelectric material.

10

105. A method according to any of the claims 101-103, wherein said oxide(s) are an oxygen ion conducting oxide(s) such as $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$, LaGaO_3 , or doped ZrO_2

106. A method according to any of the claims 101-58, wherein said primary particles
15 formed are carbide(s) and/or nitride(s) and/or sulphides and/or borides and/or hydrides and/or halogenides.

107. An apparatus comprising means according to any preceding claims thereby being adapted to carry out the method according to any of the preceding claims.

20

108. A process comprising steps according to a method of any of the preceding claims.

109. A product produced from a method according to any of the preceding claims.

25

30

35